Supporting Information for

Pd(II)-catalyzed C-H Activation and C-C Coupling/Cyclization of Benzamidine and Terminal Alkynes using an internal oxidant

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General Methods:

$^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ or DMSO-$d_6$ solutions on a Bruker AVANCE 400 MHz spectrometer. High resolution mass spectra were obtained on a Waters Micromass GCT facility. HOTf was purchased from Alfa Aesar. All other reagents and solvents were used as is from commercial sources. Unless noted below, all other compounds have been reported in the literature or are commercially available.

**General Pd(OAc)$_2$-Catalyzed C-H activation and C-C coupling/cyclization reaction Procedure:**

A round bottom flask (50 mL) was charged with benzamidine (1 mmol, 1 equiv), phenylacetylene, Pd(OAc)$_2$ (5 mol%), HOTf (5 mol%), Cu(OAc)$_2$ (20 mmol%) as in toluene (5 mL). The mixture was stirred at 130 °C for 4 hours, the reaction was cooled down to room temperature, diluted with 10 ml dichloromethane and washed with 10 ml H$_2$O. The aqueous layer was extracted twice with dichloromethane (10 ml) and the combined organic phase was dried over Na$_2$SO$_4$. After evaporation of the solvents, the residue was purified by silica gel chromatography (dichloromethane/pet. ether).
The data of selected spectra

6-Methyl-4-phenyl-quinoline \((3c)\): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) ppm: 8.11 - 8.15 (t, 3H), 8.06 (d, \(J = 8.4\) Hz, 1H), 7.83 (d, \(J = 8.4\) Hz, 1H), 7.43 - 7.58 (m, 5H), 2.54 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) ppm: 160.7, 156.1, 146.8, 136.1, 135.4, 132.4, 131.9, 129.2, 128.8, 126.9, 126.3, 118.5, 114.2, 21.6; HRMS (EI) Calcd. for C\(_{16}\)H\(_{13}\)N: [M\(^+\)], 219.1048. Found: m/z 219.1052.

6-Methoxy-4-phenyl-quinoline \((3e)\): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) ppm: 8.06 - 8.14 (t, 4H), 7.83 (d, \(J = 8.4\) Hz, 1H), 7.50 - 7.53 (t, 2H), 7.43 - 7.46 (m, 1H), 7.37 - 7.40 (m, 1H), 7.09 (d, \(J = 2.8\) Hz, 1H), 3.94 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) ppm: 157.7, 155.1, 144.4, 139.8, 135.6, 131.2, 129.0, 128.8, 127.3, 122.4, 119.3, 114.1, 105.0, 55.6; HRMS (EI) Calcd. for C\(_{26}\)H\(_{13}\)NO: [M\(^+\)], 235.0997. Found: m/z 235.0995.

7-Fluoro-4-phenyl-quinoline \((3f)\): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) ppm: 8.13 - 8.18 (m, 3H), 7.77 - 7.83 (m, 3H), 7.47 - 7.54 (m, 3H), 7.24 - 7.32 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) ppm: 164.5, 162.1, 158.3, 149.2, 139.3, 136.7, 129.6, 129.5, 129.4, 128.9, 127.6, 124.2, 118.3, 116.9, 116.6, 113.4, 113.2; HRMS (EI) Calcd. for C\(_{15}\)H\(_{10}\)NF: [M\(^+\)], 223.0797. Found: m/z 223.0794.

6-Fluoro-4-phenyl-quinoline \((3g)\): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) ppm: 8.13 - 8.18 (m, 4H), 7.87 (d, \(J = 8.8\) Hz, 1H), 7.41 - 7.54 (m, 5H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) ppm: 161.6, 159.1, 156.7, 145.4, 139.4, 136.2, 132.2, 129.4, 128.9, 127.9, 127.5, 120.0, 119.7, 110.4; HRMS (EI) Calcd. for C\(_{15}\)H\(_{10}\)NF: [M\(^+\)], 223.0797. Found: m/z 223.0792.

2-Phenylquinoline \((4a)\): \(^1\)H NMR \(\delta\) 7.46 (t, \(J = 7.8\) Hz, 1H), 7.50 - 7.58 (m, 3H), 7.73 (t, \(J = 7.8\) Hz, 1H), 7.83 (d, \(J = 8.1\) Hz, 1H), 7.88 (d, \(J = 8.6\) Hz, 1H), 8.13 - 8.26 (m, 4H); \(^{13}\)C NMR \(\delta\) 118.90, 126.15, 127.05, 127.33, 127.44, 128.70, 129.18, 129.51, 129.62, 136.61, 139.55, 148.13, 157.17; HRMS (EI) Calcd. For C\(_{15}\)H\(_{11}\)N: [M\(^+\)], 205.0891. Found: m/z 205.0892.

2-(3-Methylphenyl)quinoline \((4b)\): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) ppm: 8.15 - 8.22 (m,
2H), 8.01 (s, 1H), 7.92 (d, \( J = 7.6 \) Hz, 1H), 7.85 (dd, \( J = 2.7, 8.6 \) Hz, 1H), 7.81 (d, 1H, \( J = 8.1 \) Hz), 7.68 - 7.75 (m, 1H), 7.48 - 7.54 (m, 1H), 7.41 (dt, \( J = 2.6, 7.6 \) Hz, 1H), 7.28 (d, \( J = 7.6 \) Hz, 1H), 2.48 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) ppm: \( \delta 157.4, 148.1, 139.5, 138.3, 136.5, 130.0, 129.6, 129.5, 128.6, 128.1, 127.3, 127.0, 126.1, 124.6, 119.0, 21.7; HRMS (EI) Calcd. for C\(_{16}\)H\(_{13}\)N: [M\(^+\)], 219.1048. Found: m/z 219.1051.

2-(3-Nitrophenyl)quinoline (4c): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) ppm: 9.0 (s, 1H), 8.44 (d, \( J = 6.8 \) Hz, 1H), 8.10 (m, 3H), 7.48 - 7.83 (m, 5H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) ppm: \( \delta 154.4, 149.9, 137.5, 135.8, 135.2, 133.4, 130.2, 129.8, 127.6, 127.1, 123.9, 122.4, 118.4, 116.4, 116.1; HRMS (EI) Calcd. for C\(_{15}\)H\(_{10}\)N\(_2\)O\(_2\): [M\(^+\)], 250.0742. Found: m/z 250.0749.

2-(4-Methylphenyl)quinoline (4d): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) ppm: 8.15 (d, \( J = 4.1 \) Hz, 1H), 8.00 - 8.05 (m, 3H), 7.60 - 7.75 (m, 3H), 7.35 - 7.45 (m, 1H), 7.25 (d, \( J = 8.1 \) Hz, 2H), 2.36 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) ppm: \( \delta 156.9, 148.0, 139.1, 136.6, 136.4, 139.4, 129.3, 128.0, 127.3, 127.2, 126.8, 125.8, 118.5, 21.1; HRMS (EI) Calcd. for C\(_{16}\)H\(_{13}\)N: [M\(^+\)], 219.1048. Found: m/z 219.1052.

2-(4-Nitrophenyl)quinoline (4e): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) ppm: 8.21 (d, \( J = 8.4 \) Hz, 1H), \( \delta 8.11 \) (d, \( J = 8.8 \) Hz, 1H), 7.78 - 7.84 (m, 2H), 7.67 - 7.72 (m, 1H), 7.46 - 7.57 (m, 2H), 6.84 - 7.03 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) ppm: \( \delta 154.6, 148.3, 145.5, 137.4, 131.0, 130.1, 129.6, 129.2, 129.0, 128.7, 128.2, 120.1, 119.7; HRMS (EI) Calcd. for C\(_{15}\)H\(_{10}\)N\(_2\)O\(_2\): [M\(^+\)], 250.0742. Found: m/z 250.0748.

2-Cyclohexylquinoline (4f): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) ppm: 8.06 (d, \( J = 8.4 \) Hz, 2H), 7.75 (d, \( J = 8.0 \) Hz, 1H), 7.64 - 7.68 (t, 1H), 7.44 - 7.47 (t, 1H), 7.31 (d, \( J = 8.4 \) Hz, 1H), 2.88 - 2.96 (m, 1H), 2.01 (m, 2H), 1.86 - 1.90 (M, 2H), 1.78(M, 1H), 1.57 - 1.67 (m, 2H), 2.88 - 2.96 (m, 1H), 1.86 - 1.90 (M, 2H), 1.78(M, 1H), 1.57 - 1.67 (m, 2H), 2.88 - 2.96 (m, 1H), 1.86 - 1.90 (M, 2H), 1.78(M, 1H), 1.57 - 1.67 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) ppm: 166.9, 147.8, 136.4, 129.3, 128.9, 127.5, 127.0, 125.6, 119.6, 47.6, 32.9, 26.6, 26.1; HRMS (EI) Calcd. for C\(_{18}\)H\(_{17}\)N: [M\(^+\)], 211.1361. Found: m/z 211.1364.
8-Methyl-2-phenylquinoline (4g): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm: 8.22 - 8.28 (m, 2H), 8.14 (d, 1H, $J = 8.6$ Hz), 7.86 (d, 1H, $J = 8.6$ Hz), 7.63 (d, $J = 7.2$ Hz, 1H), 7.55 (d, $J = 7.2$ Hz, 1H), 7.51 (t, $J = 7.4$ Hz, 2H), 7.44 (q, 1H), 7.38 (t, $J = 7.2$ Hz, 1H), 2.90 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm: 155.5, 147.1, 139.8, 137.6, 136.9, 129.6, 129.2, 128.7, 127.4, 127.1, 126.0, 125.4, 118.2, 17.9; HRMS (EI) Calcd. for C$_{16}$H$_{13}$N: [M$^+$], 219.1048. Found: m/z 219.1044.

4-Methyl-2-phenylquinoline (4h): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm: 8.13 (d, $J = 8.8$ Hz, 1H), 8.01 (s, 1H), 7.77 (d, $J = 8.0$ Hz, 1H), 7.64 - 7.68 (m, 1H), 7.58 - 7.60 (m, 2H), 7.41 - 7.53 (m, 4H), 2.46 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm: 152.4, 148.1, 145.4, 136.7, 129.9, 129.3, 128.6, 128.1, 127.5, 127.2, 126.1, 125.9, 117.7; HRMS (EI) Calcd. for C$_{16}$H$_{13}$N: [M$^+$], 219.1048. Found: m/z 219.1046.

2-p-tolyl-6-methylquinoline (4i): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm: 8.14 (d, $J = 8.5$ Hz, 1H), 8.07 (d, $J = 8.5$ Hz, 3H), 7.84 (d, $J = 8.5$ Hz, 1H), 7.58 (q, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 2.57 (s, 3H), 2.46 (s, 3H); $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ ppm: 156.5, 147.6, 146.8, 143.8, 139.2, 136.0, 131.9, 129.5, 129.3, 128.8, 127.3, 126.3, 118.8, 21.6, 21.3; HRMS (EI) Calcd. for C$_{17}$H$_{15}$N: [M$^+$], 233.1204. Found: m/z 233.1199.
"\(^1\)H and \(^{13}\)C spectra of selected spectra"